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# Improving the Regeneration of Carbonated MEA Solutions

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### ABSTRACT

Investigators at NRL have attempted to increase the effectiveness of the CO<sub>2</sub> Scrubber, currently used in nuclear submarines, to reduce the CO<sub>2</sub> levels in the atmospheres. Redesigns of parts of the present unit could show appreciable increases in efficiency. To approach the desired level of 0.5% CO<sub>2</sub> in the submarine atmosphere, a size redesign will be required. The data revealed that a redesign of the stripper on the present size unit could give nearly twice the current stripping efficiency.

### PROBLEM STATUS

This is a final report on the MEA stripping phase of the problem.

### AUTHORIZATION

NRL Problem C08-05  
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## IMPROVING THE REGENERATION OF CARBONATED MEA SOLUTIONS

### BACKGROUND

Investigations reveal that the concentration of  $\text{CO}_2$  in nuclear submarine atmospheres may be further reduced by increasing the effectiveness of the monoethanolamine (MEA) stripping operation in the  $\text{CO}_2$  Removal Plant. If the desorber, over a period of time, can discard more  $\text{CO}_2$  than is being absorbed, the  $\text{CO}_2$  loading, or V/v of the rich solution,\* will equilibrate at a level significantly lower than presently maintained by ship-board units. Eventually, the absorption rate will again equal the desorption rate, but since the absorber is now able to function more effectively with a leaner solution, the overall performance of the MEA- $\text{CO}_2$  system is improved.

A redesigned stripper could make the present system more satisfactory, but if the allowable continuous exposure level of  $\text{CO}_2$  is reduced to 0.5%, the volume of air handled by the  $\text{CO}_2$  Removal Plant will have to be increased. (It is obvious that for 140 men, producing 14 lb/hr of  $\text{CO}_2$ , a goal of 0.5%  $\text{CO}_2$  as the ambient  $\text{CO}_2$  level cannot be realized if only 250 cu ft/min of air are processed in each  $\text{CO}_2$  Removal Plant. If it were possible to remove all of the  $\text{CO}_2$  from 250 cu ft/min of air containing 0.5%  $\text{CO}_2$ , the removal rate would only be 9.2 lb/hr  $\text{CO}_2$ .) Any increase in the volume of air processed will require greater efficiency from the stripping unit.

In the present system the pressure drop on the discharge side of the absorber is probably larger than it should be. The discharge air duct from some absorbers is placed along the inside wall of the absorber and then flares out as it approaches the packing support. If this flared-out area is too small, there will be more mist formation than usual, and if it is too large, the pressure drop of the air flowing across the remaining packing support area will increase. An improvement over this situation is certainly possible. A recommended change would be an annular duct which yields an uncluttered absorption space by being located between the shell of the packed section and a new outer shell. Even with the same external dimensions, the redesigned absorber would still have about the same packed volume and a possibility of a simplified discharge ducting. Since a large area can be obtained with only a few inches of thickness around the absorber, mist formation might be more easily discouraged at a lower pressure drop.

A redesigned stripper will be necessary if each absorber is to process an estimated minimum of 500 to 600 cu ft/min of air. Other improvements will also be required in the absorber since Raschig rings are not noted for efficiency at higher gas and liquid flow rates (1,2). The choice of the best packing material is not easy. Stainless-steel Pall rings may be too expensive, and economical plastic Pall rings, which are better than Raschig rings, although not as effective as the metal rings, were probably rejected because of possible attrition and breakage. Because the plastic Pall rings are economical and better than Raschig rings, it is recommended that they be tried with a suitable hold-down screen. Although the Pall rings give a lower pressure drop than equal-sized Raschig

\*The ratio V/v refers to the volume of  $\text{CO}_2$ , at standard conditions, absorbed per unit volume of MEA solution at room temperature. Rich and lean are relative terms in regard to  $\text{CO}_2$  content of the MEA solution depending on the degree of carbonation before and after regeneration.

rings under the same conditions, the large volume of air handled dictates an increase in packing size. The choice of 1-inch Pall rings over 1/2-inch Raschig rings would mean the loss of some surface area in the packing, but this disadvantage would surely be offset by an increase in the removal rate of  $\text{CO}_2$ .

It is difficult to assign a typical, rich V/v to a MEA solution aboard ship. The atmosphere, the equipment, and the operation and maintenance of that equipment are all somewhat different for each ship. Another complication is that simultaneous operation of two scrubbers is frequently required to keep the  $\text{CO}_2$  level near 1% since the number of personnel aboard submarines often exceeds the design capabilities of the MEA- $\text{CO}_2$  system. The  $\text{CO}_2$  content of either scrubber solution would then be expected to decrease. Even for single scrubber operation, several factors can affect the V/v. The absorber, for instance, tends to remove more  $\text{CO}_2$  at higher ambient concentrations, but this removal is opposed by a decrease in efficiency at a higher V/v. The output of the desorber also varies since, for a given amount of energy, it is much easier to desorb  $\text{CO}_2$  if the feed solution to the desorber is highly loaded.

Figure 1, replotted from data obtained by P.R. Gustafson of this Laboratory, shows a decrease in absorption performance by 4.5N MEA with an increase in  $\text{CO}_2$  content. This plot represents a batch test using 50 ml of 88°F solution through which 3.3 lpm of air containing 1%  $\text{CO}_2$  were passed. The concentration of  $\text{CO}_2$  in the effluent was recorded with respect to time. Under these conditions, the low effluent concentrations of  $\text{CO}_2$  reveal a much greater absorption efficiency than could be expected from a full-size absorber. Whatever the relationship between the effluent concentration of  $\text{CO}_2$  from a shipboard scrubber and the V/v of its absorber solution, it is obvious that as low a V/v as possible is required within the limits of a reasonable energy expenditure in regeneration.

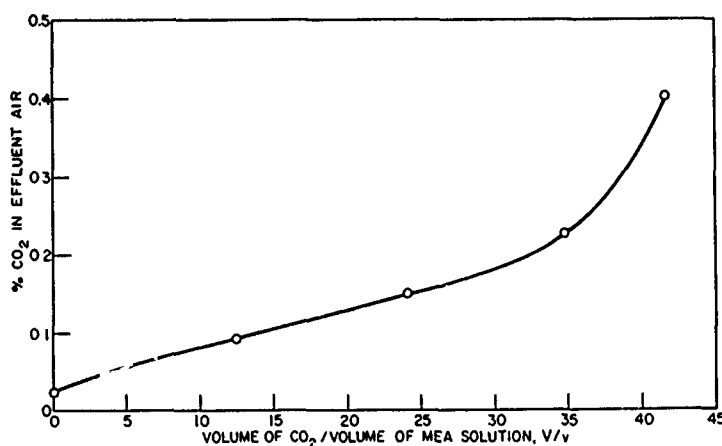


Fig. 1 - Effluent concentration of  $\text{CO}_2$  from batch absorption of 1%  $\text{CO}_2$  in air by 4.5N MEA; 50 ml MEA solution at 88°F; 3.3 lpm STP air flow;  $(V/v)_{\text{sat.}} = 50.4$

An additional, important factor is the extent to which a MEA solution may be carbonated before it becomes ineffective as an absorber. A 4.5N MEA solution saturated with  $\text{CO}_2$  (as carbonate) will have a V/v of 50.4. According to Mason and Dodge (3), the equilibrium partial pressure of  $\text{CO}_2$  over MEA solutions is negligible until 80% of the MEA is converted to carbonate. Therefore, the V/v of the solution in the absorber should

never exceed 40.3, which is 80% of 50.4. Figure 1, however, shows an increase in the slope of the curve at a V/v of 35. This deviation is probably due to a combination of factors, such as an increase in viscosity and decrease in pH, finally contributing to an increase in resistance to liquid-phase diffusion of  $\text{CO}_2$ . The maximum V/v tolerated for solutions weaker than 4.5N requires even greater efficiency from the desorber. In the case of a 4N MEA solution, the saturated V/v is 44.8, and 0.8 of that value is 35.8. If the effluent  $\text{CO}_2$  curve is similar, the operating condition should be a V/v under 30.

### SHIPBOARD DESORBER

The regeneration of carbonated 4.5N MEA solutions requires a temperature of about  $285^\circ\text{F}$ . The present shipboard equipment must be operated at a pressure of around 35 psig to obtain this boiling point. Electrical heaters provide direct heating of the solution in the reboiler. Steam and  $\text{CO}_2$ , released by boiling, pass upward and countercurrently to hot and rich MEA which is sprayed over a packed section. Additional  $\text{CO}_2$  is then stripped from the preheated MEA by the steam, which is subsequently separated from the  $\text{CO}_2$  by condensation.

The flow of  $\text{CO}_2$  from the desorber is regulated by a backpressure valve which maintains the desired pressure. Another important unit is a float valve which releases hot, lean MEA to a heat exchanger in response to changes in liquid level in the reboiler. This operation is done indirectly since the stem of the float valve operates on chilled MEA to avoid flashing under pressure reduction.

To improve the process, changes in the reboiler would be most beneficial. The principle behind these changes is the reduction of the partial pressure of  $\text{CO}_2$  by evolution of steam in suitably designed equipment.

### LABORATORY DESORBER

The laboratory reboiler, as shown in Fig. 2, was inclined slightly so that a vapor space was formed along the length of the tube. Preheated, rich MEA was introduced at the bottom of the raised end of the tube and flowed out through an opening in the upper part of the lower end. A 2000-watt immersion heater with a stainless-steel sheath was folded and placed so as to provide heat throughout the tube. The heater was held below the liquid surface by two baffles, with openings at the top and bottom to permit gas and liquid flow, which discouraged thermal mixing of the rich and lean MEA. Additional energy was provided by four 650-watt ceramic heaters mounted externally on the bottom of the tube-reboiler. The solution, in passing through the tube, was heated to boiling, and the steam produced, flowing countercurrent to the rich MEA, swept the evolved  $\text{CO}_2$  away. A particularly effective location was the lean MEA exit, where the steam had the best opportunity to reduce the partial pressure of  $\text{CO}_2$  over the MEA because of the diminishing volume of vapor space created by tube geometry.

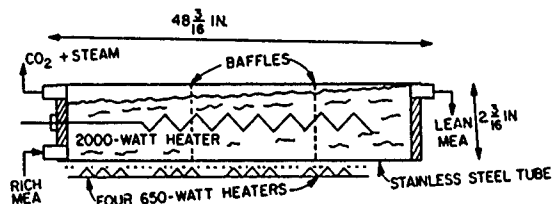


Fig. 2 - Laboratory tube reboiler

The scaling of the laboratory desorber was based on early Mark I CO<sub>2</sub> Removal Plants (Units 34 through 39). The volume of the tube-reboiler is about 1/8 the volume of a typical Mark I desorber less the volumes associated with the condenser and float tank. Because of later modification of shipboard units, these dimensional scale considerations are not as pertinent as when designed. However, the ratio of the flow rate of MEA solution to the working volume of the laboratory desorber still compares favorably with all shipboard units.

#### RUN-PROCEDURE OF LABORATORY DESORBER

A continuous method of operation was used for each run as shown in Fig. 3. About 25 gallons of precarbonated-MEA solution ("dry-ice" was convenient for quickly saturating some of the solutions and had no discernibly harmful effects) were preheated to 180-190°F in a stainless-steel storage tank. This preheated MEA was then transferred to the reboiler by means of air pressure maintained a few pounds above the reboiler pressure. The rate of flow of rich MEA, 1/8 gal/min, was adjusted by a needle valve and monitored on a Kel-F rotameter. For a given valve opening, the flow was a function of the pressure difference between the constant air supply pressure and the pressure maintained in the desorber. The steadiness of MEA flow was satisfactory, since the variations in desorber pressure were minor. A heater cable, controlled by an adjustable transformer, was wrapped around the line ahead of the reboiler to provide heat and to control the temperature of the rich MEA at about 210°F. The laboratory unit was, therefore, at a disadvantage since the temperature of the feed stream to a full-size stripper may be as high as 258°F. At temperatures above 210°F, enough CO<sub>2</sub> was released, even at moderate CO<sub>2</sub> loadings of the MEA, to disrupt the even flow of MEA. It should be noted that the flow system for the laboratory stripper did not include a packed section.

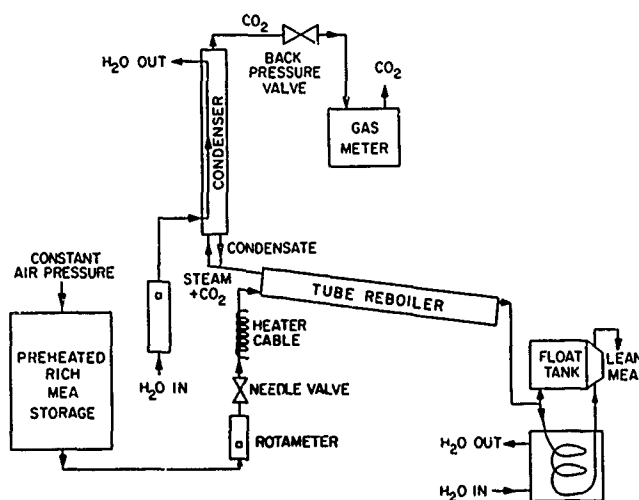


Fig. 3 - Batch-continuous regeneration of carbonated MEA

In the experimental apparatus the float valve was used mainly to control the flow of MEA leaving the system and was mounted in a separate tank below the tube reboiler. A small vent tube between the vapor spaces of the float tank and reboiler was required to equalize the pressure. Since the MEA in the float tank could be cooled to as low as 140°F,



some reabsorption of  $\text{CO}_2$  was possible and would lead to conservative results. This effect was shown to be negligible by a mass balance involving the  $\text{CO}_2$  evolved, the flow rate of MEA, and the change in  $\text{CO}_2$  content of the MEA.

During a run, the system was operated until it reached a thermal steady state, a condition which required a constant flow rate of all fluids. At this point, lean MEA was collected for a measured time (10 min), during which the NTP volume of  $\text{CO}_2$  evolved was obtained using a calibrated gas meter. A mass balance of the system showed, on the average, a 95% agreement between the measured evolved  $\text{CO}_2$  and the analyzed  $\text{CO}_2$  loadings of the rich and lean MEA.

A double-pipe heat exchanger was used to condense the steam inside the inner tube. Tap water, at a constant flow rate of 1.1 gal/min, was used as a cooling medium. The temperature of the water, before and after the condenser, was recorded. Samples of the condensate usually showed about 0.6N MEA, some of which could have been due to entrainment. A smaller amount of condensed MEA would be expected.

The values of  $V/v$  of the MEA solutions were determined volumetrically by evolution of  $\text{CO}_2$ . The  $\text{CO}_2$  was released from 1 to 2 ml samples by a 50% phosphoric acid solution in a reaction tube. The evolved gas was then displaced by mercury into a volumetric burette, where it was collected over an acidified sodium sulphate solution saturated with  $\text{CO}_2$ . The volume of  $\text{CO}_2$ , equilibrated with respect to barometric pressure and to the temperature of the confining solution, was then recorded and corrected to standard conditions. These determinations were made with an agreement of 0.5  $V/v$  or less.

## RESULTS AND DISCUSSION

Data taken with the tube-reboiler are shown in Table 1. The 14 runs are arranged in three groups according to the  $V/v$  values of the rich MEA. The  $V/v$  of the lean MEA may be obtained by subtracting the change in  $V/v$  from the  $V/v$  of the rich MEA. Condenser duty was obtained from the volume flow of cooling water and its temperature increase, which was assumed to be due only to condensation of steam. Condenser duty on a shipboard desorber would be about 24,000 Btu/hr. The expected outputs of  $\text{CO}_2$  of a submarine  $\text{CO}_2$  stripper, operating at the same efficiencies achieved in the laboratory, are listed in the last column. (In making comparisons to a shipboard unit it should be noted that 10 lpm of  $\text{CO}_2$  is equivalent to 2.6 lb/hr of  $\text{CO}_2$ .) All results were obtained without the use of a packed section.

Let it be assumed that the  $V/v$  of the rich solution aboard ship varies from 30 to 35. If the average removal rate of  $\text{CO}_2$  from the submarine is 11 lb/hr over this range and a flow rate of 1 gal/min of rich MEA is used for regeneration, the change in  $V/v$  of the solution passing through the desorber will be 11.2. The stripping efficiency, which may be defined as the ratio of the change in  $V/v$  to the  $V/v$  of the rich MEA, would then vary from 38% to 32%.

Although the removal rate of  $\text{CO}_2$  by the shipboard desorber will increase with the  $\text{CO}_2$  loading of the MEA, the maximum rate appears to be 14 lb/hr or less of  $\text{CO}_2$  at an ambient  $\text{CO}_2$  level of 1.5%. In Table 1 the results of Run 20 in the first group indicate a potential yield of 26.2 lb/hr of  $\text{CO}_2$  by a full-size desorber of this design. This yield is an 87% increase over the present efficiency of submarine strippers. The improvement in efficiency is less in the middle group. Here, the best yield of 17.5 lb/hr of  $\text{CO}_2$  would be 59% better than 11 lb/hr of  $\text{CO}_2$ . In the middle group Run 11 is least productive, but despite a relatively lower energy input, the change in  $V/v$ , 12.7, and the efficiency, 40%, are both still favorable. Runs 10 and 11 were made using only the 2000-watt heater, while the other runs were made with some additional external energy. With an increase in energy input, as shown by the increase in condenser duty, the stripping efficiency was

increased to 55%. Runs 16 and 13 show that an increase in the steam-to-CO<sub>2</sub> ratio is also helpful. The runs at a higher pressure, 35 psig, and a higher temperature, 283°F, are usually the best in each group.

Table 1  
Results of Desorbing CO<sub>2</sub> From Carbonated 4.3N MEA  
in the Tube Reboiler (275°F and 30 psig)

Run No.	(V/v) Rich	Change in V/v	%m CO <sub>2</sub> dry (Stp)	Condenser Duty (Btu/hr)	Lb Steam Lb CO <sub>2</sub>	Percent Efficiency Change in V/v × 100 (V/v) Rich	Lb/hr CO <sub>2</sub> (if full scale)
10	43.3	18.2	8.8	1400	0.7	42	18.3
19*	41.6	21.6	10.3	2500	1.9	52	21.4
17	40.0	21.4	9.7	3000	1.3	54	20.2
18	43.5	24.9	11.7	5500	1.9	57	24.4
20*	45.5	27.7	12.6	6000	2.0	61	26.2
11	31.9	12.7	6.3	2200	1.4	40	13.1
16	31.4	13.8	6.5	6000	2.5	44	13.5
12	32.1	14.2	7.1	5500	3.0	44	14.8
15	31.7	16.0	7.2	4500	2.6	51	15.0
13	33.0	15.8	8.0	5500	3.1	48	16.7
21*	34.3	19.0	8.4	3600	1.8	55	17.5
14	25.0	10.7	5.0	7100	5.9	43	10.4
22*	18.5	8.4	3.5	7700	9.3	45/39	7.3
23a	19.1	6.9	3.0	6000	8.4	36/33	6.2
23b	19.1	5.6	2.2	3000	6.3	29/21	4.6

\* 35 psig and 283°F.

In Runs 14, 22, 23a, and 23b, the steam-to-CO<sub>2</sub> ratio are the highest. This is due, in part, to a smaller CO<sub>2</sub> evolution and, in part, to the fact that it takes energy to release CO<sub>2</sub>; since less CO<sub>2</sub> was released, more energy was available for steam generation. (The Arrhenius energy of activation of the decomposition of MEA-CO<sub>2</sub> (27.5 kcal/g mol) was calculated over the temperature range of 230 to 285°F by M. Matsuda (4).) The lean V/v in the last group also seems to be approaching a limit of around 10. Runs 22 and 23 show that it may not be practicable to exceed a steam-to-CO<sub>2</sub> ratio of 9.3 because the excess steam with these very lean solutions may no longer be as effective or economical. (At 35 psig pressure, it requires 924 Btu to form one pound of steam.) An undesirable excess of steam also penalizes the already hard-working condenser.

The material balances for Runs 22 and 23 were not as accurate as in the other runs, so a lower limit of efficiency was also given.

The results show, not surprisingly, that regeneration of nearly saturated solutions is easier than regeneration of unsaturated solutions. Unfortunately, a simple method of separating carbonated MEA from MEA is not available.

#### CONCLUSIONS AND RECOMMENDATIONS

These results show that a redesign of the stripper could benefit the overall performance of the present CO<sub>2</sub> Removal Plant. An increase in energy input would be required for optimum results. At least one additional heater should be added to provide more steam, and the operating pressure should be 35 psig. While a larger condenser would

almost certainly be needed, the additional space required for the condenser could be provided by decreasing the height of the packing in the stripper.

A possible design of the stripper reboiler is shown in Fig. 4. Here, the tube-reboiler becomes a continuous length of alternating sealed passageways, baffled to reduce liquid sloshing. Preheated MEA, after passing over a shorter packed section, would enter the reboiler at the float location. The heaters and float valve could be attached to a removable panel sealed by a gasket from internal and external leaks. All these changes, including a redesigned stripper, should, of course, be tried in a full-size, land-based CO<sub>2</sub> Removal Plant.

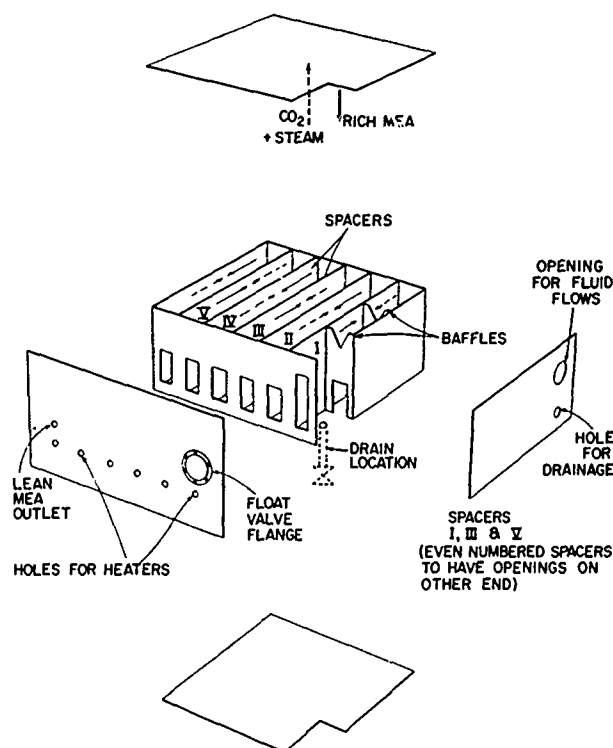


Fig. 4 - A possible reboiler design

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<p>Investigators at NRL have attempted to increase the effectiveness of the CO<sub>2</sub> Scrubber, currently used in nuclear submarines, to reduce the CO<sub>2</sub> levels in the atmospheres. Redesigns of parts of the present unit could show appreciable increases in efficiency. To approach the desired level of 0.5% CO<sub>2</sub> in the submarine atmosphere, a size redesign will be required. The data revealed that a redesign of the stripper on the present size unit could give nearly twice the current stripping efficiency.</p>			

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Carbon dioxide Absorption rate Desorption rate CO <sub>2</sub> Scrubber Monoethanolamine						